

# Vibrational Properties of Double Tungstates of the $M^I M^{III}(\text{WO}_4)_2$ Family ( $M^I = \text{Li, Na, K}$ ; $M^{III} = \text{Bi, Cr}$ )

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Infrared and Raman spectra of polycrystalline double tungstates  $M^I M^{III}(\text{WO}_4)_2$ , where  $M^I = \text{Li, Na, K}$ ;  $M^{III} = \text{Bi, Cr}$ , were measured at room temperature in the range 30–1000  $\text{cm}^{-1}$ . Factor group analysis was performed and the results of these calculations were used to determine the nature of the observed modes. The coordination around the tungsten atom depends on the type of cation and is either tetrahedral or octahedral. Profound differences between vibrational spectra of tetrahedral and octahedral systems are observed. Comparing IR and Raman spectra, we assigned the vibrations above 250  $\text{cm}^{-1}$  as internal tungsten–oxygen vibrations and those below 250  $\text{cm}^{-1}$  as external vibrations. © 1995 Academic Press, Inc.

## 1. INTRODUCTION

Double alkali metal bismuth tungstates are prospective media for quantum electronics. In the past years a few papers related to the luminescence properties of  $\text{NaBi}(\text{WO}_4)_2$  have been published (1–3). The present paper deals with the IR and Raman spectra of alkali metal bismuth and alkali metal chromium tungstates. Because of the prospective application of the  $M^I \text{Cr}_x \text{Bi}_{1-x}(\text{WO}_4)_2$  systems as quantum generators, the stability and properties of  $M^I \text{Bi}(\text{WO}_4)_2$  crystals are analyzed.

## 2. EXPERIMENTAL

The crystals were grown by the thermal method developed by Borisov and Klevtsova (4) and Klevtsov *et al.* (5). Infrared spectra in the range 1000–400  $\text{cm}^{-1}$  were recorded in a Perkin–Elmer 2000 FTIR spectrometer at a resolution of 1  $\text{cm}^{-1}$  and in the far-infrared range at a resolution of 2  $\text{cm}^{-1}$ . Raman spectra were observed in back-scattering geometry in a Perkin–Elmer 1760X FTIR spectrometer, equipped with a Raman module. Excitation was performed with a YAG:Nd<sup>3+</sup> laser ( $\lambda = 1064 \text{ nm}$ ) at a power of 300 mW for alkali metal–bismuth double tungstates and 150 mW for alkali metal–chromium double

tungstates. All spectra were recorded with a resolution of 2  $\text{cm}^{-1}$  using an InGaAs detector operating at the temperature of liquid nitrogen. Since the Perkin–Elmer 1760X FTIR spectrometer enabled us to record Raman spectra only above 200  $\text{cm}^{-1}$ , additional measurements in the range 300–30  $\text{cm}^{-1}$  were carried out in a double DFS 24 spectrometer with a photon counting detection system (cooled RCA C 31034-02 photomultiplier tube). The excitation source was the 488-nm line of an argon ion laser. The output power was 150 mW and the resolution was 2  $\text{cm}^{-1}$ . The Cr crystals were very dark and it was not possible to detect low wavenumber RS spectra.

X-ray diffraction was performed using  $\text{CuK}\alpha$  radiation in a Siemens D5000 powder diffractometer with a helium low-temperature attachment.

## 3. RESULTS AND FACTOR GROUP ANALYSIS

### 3.1. $\text{NaBi}(\text{WO}_4)_2$ Tungstate of Scheelite-Type Structure

$\text{NaBi}(\text{WO}_4)_2$  crystallizes in the tetragonal space group  $I4_1/a = C_{4h}^6$  with two molecules per unit cell and lattice parameters  $a = 5.28 \text{ \AA}$  and  $c = 11.50 \text{ \AA}$  (6). This structure is of the scheelite type because the  $\text{Na}^+$  and  $\text{Bi}^{3+}$  ions randomly replace the  $\text{Ca}^{2+}$  ions of the  $\text{CaWO}_4$  (6). The tungsten (VI) ions are tetrahedrally coordinated to the oxygen, forming isolated  $\text{WO}_4^{2-}$  units occupying the sites of the  $S_4$  symmetry. This type of structure is characterized by the following coordination numbers (CN) and site symmetries (SS):  $\text{CN}(\text{Na}^+) = 8$ ,  $\text{CN}(\text{Bi}^{3+}) = 8$ , and  $\text{CN}(\text{W}^{6+}) = 4$ ;  $\text{SS}(\text{Na}^+) = C_2$ ,  $\text{SS}(\text{Bi}^{3+}) = C_2$ , and  $\text{SS}(\text{W}^{6+}) = S_4$ . Since the unit cell contains two equivalent compounds, the primitive cell with only one formula unit was selected as the basis for factor group analysis (FGA). The results of these calculations are summarized in Table 1. The IR and Raman spectra of this compound are presented in Fig. 1. Band frequencies and their assignments are listed in Table 2.

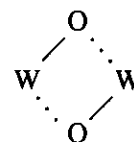
TABLE 1  
Factor Group Analysis for  $\text{NaBi}(\text{WO}_4)_2$  Crystal ( $I4_1/a$ ,  $Z = 2$ )

$C_{4h}$	$E$	$C_4(z)$	$C_2$	$C_4^3$	$i$	$S_4^3$	$\sigma_h$	$S_4$	Unit-cell modes					Activity	
									$n(N)$	$n(T)$	$n(T')$	$n(L)$	$n(\text{int})$	IR	Raman
$A_g$	1	1	1	1	1	1	1	1	3	0	0	1	2	—	$XX + YY, ZZ$
$B_g$	1	-1	1	-1	1	-1	1	-1	5	0	2	0	3	—	$XX - YY, XY$
$E_g$	1	$i$	-1	- $i$	1	$i$	-1	- $i$	5	0	2	1	2	—	$XZ, YZ$
	1	- $i$	-1	$i$	1	- $i$	-1	$i$	5	0	2	1	2		
$A_u$	1	1	1	1	-1	-1	-1	-1	5	1	1	0	3	Z	—
$B_u$	1	-1	1	-1	-1	1	-1	1	3	0	0	1	2	—	—
$E_u$	1	$i$	-1	- $i$	-1	- $i$	1	$i$	5	1	1	1	2	X, Y	—
	1	- $i$	-1	$i$	-1	$i$	1	- $i$	5	1	1	1	2		
$U_R(p)$	12	0	4	0	0	4	0	4	36	3	9	6	18		
$U_R(s)$	4	0	4	0	0	4	0	4							
$U_R(s - \nu)$	2	0	2	0	0	2	0	2							
$\chi_\rho(R)_N$	36	0	-4	0	0	-4	0	-4							
$\chi_\rho(R)_T$	3	1	-1	1	-3	-1	1	-1							
$\chi_\rho(R)_{T'}$	9	-1	-3	-1	3	-3	-1	-3							
$\chi_\rho(R)_L$	6	0	-2	0	0	2	0	2							

### 3.2. $\text{LiBi}(\text{WO}_4)_2$ Tungstate of Monoclinic $P2/n = C_{2h}^4$ Structure

$\text{LiBi}(\text{WO}_4)_2$  crystallizes in the monoclinic space group  $P2/n = C_{2h}^4$  with two molecules per unit cell and lattice parameters  $a = 10.06$ ,  $b = 6.07$ ,  $c = 4.99$  Å, and  $\beta = 92.5^\circ$  (6). This crystal is isostructural to  $\beta\text{-LiYb}(\text{WO}_4)_2$  of the wolframite-type for which  $a = 9.89$ ,  $b = 5.77$ ,  $c = 4.98$  Å, and  $\beta = 93.5^\circ$  (7) and  $\text{CN}(\text{Li}^+) = 6$ ,  $\text{CN}(\text{Yb}^{3+}) = 6$ ,  $\text{CN}(\text{W}^{6+}) = 6$ ,  $\text{SS}(\text{Li}^+) = C_2$ ,  $\text{SS}(\text{Yb}^{3+}) = C_2$ , and  $\text{SS}(\text{W}^{6+}) = C_1$ . Tungstate ions in this structure are addi-

tionally connected to each other by means of intermolecular interactions of the



type, forming chains along the  $c$  direction. The resulting coordination octahedron,  $\text{WO}_6^{6-}$ , is strongly distorted with  $\text{W-O}$  distances ranging from 1.79 to 2.27 Å. Irreducible representations and activities calculated for three-dimensional crystal vibrations are listed in Table 3, and for vibrational frequencies in Table 4. The spectra are presented in Fig. 2.

### 3.3. $\text{KBi}(\text{WO}_4)_2$ Tungstate of Monoclinic $C2/c$ Structure

$\text{KBi}(\text{WO}_4)_2$  crystallizes in the  $C2/c = C_{2h}^6$  space group with four molecules per unit cell and lattice parameters  $a = 8.25$ ,  $b = 10.60$ ,  $c = 7.62$  Å, and  $\beta = 93.8^\circ$  (6). This double tungstate is isostructural to  $\alpha\text{-KY}(\text{WO}_4)_2$ , for which  $a = 10.64$ ,  $b = 10.35$ ,  $c = 7.54$  Å, and  $\beta = 130.5^\circ$  (4, 5), and  $\text{CN}(\text{K}^+) = 12$ ,  $\text{CN}(\text{Y}^{3+}) = 8$ ,  $\text{CN}(\text{W}^{6+}) = 6$ ,  $\text{SS}(\text{K}^+) = C_2$ ,  $\text{SS}(\text{Y}^{3+}) = C_2$ , and  $\text{SS}(\text{W}^{6+}) = C_1$ . The structure of this tungstate consists of chains spread along the  $c$  axis and involving  $\text{W}_2\text{O}_8$  cores. The respective dimer  $\text{W}_2\text{O}_{10}$  contains two  $\text{WO}_6$  polyhedra joined by

TABLE 2  
IR and Raman Frequencies for Polycrystalline  $\text{NaBi}(\text{WO}_4)_2$

IR spectrum $u$ -phonons	Raman spectrum $g$ -phonons	Assignment
922w	927sh	} $\nu_1 - \nu_s(\text{WO}_4)$
910sh	907vs	
860sh	880vw	} $\nu_3 - \nu_{as}(\text{WO}_4)$
828m	815vw	
778sh	770m	
740s		} $\nu_4 - \delta_{as}(\text{WO}_4)$
407m	414vw	
395sh	386w	
294s		} $\nu_2 - \delta_s(\text{WO}_4)$
254s	328m	
210vw	193w	} $T'(\text{Na}^+)$ and $L(\text{WO}_4)$
173m		
138w	111w	} $T'(\text{Bi}^{3+})$ and $T'(\text{W}^{6+})$
99m		
83m	67m	

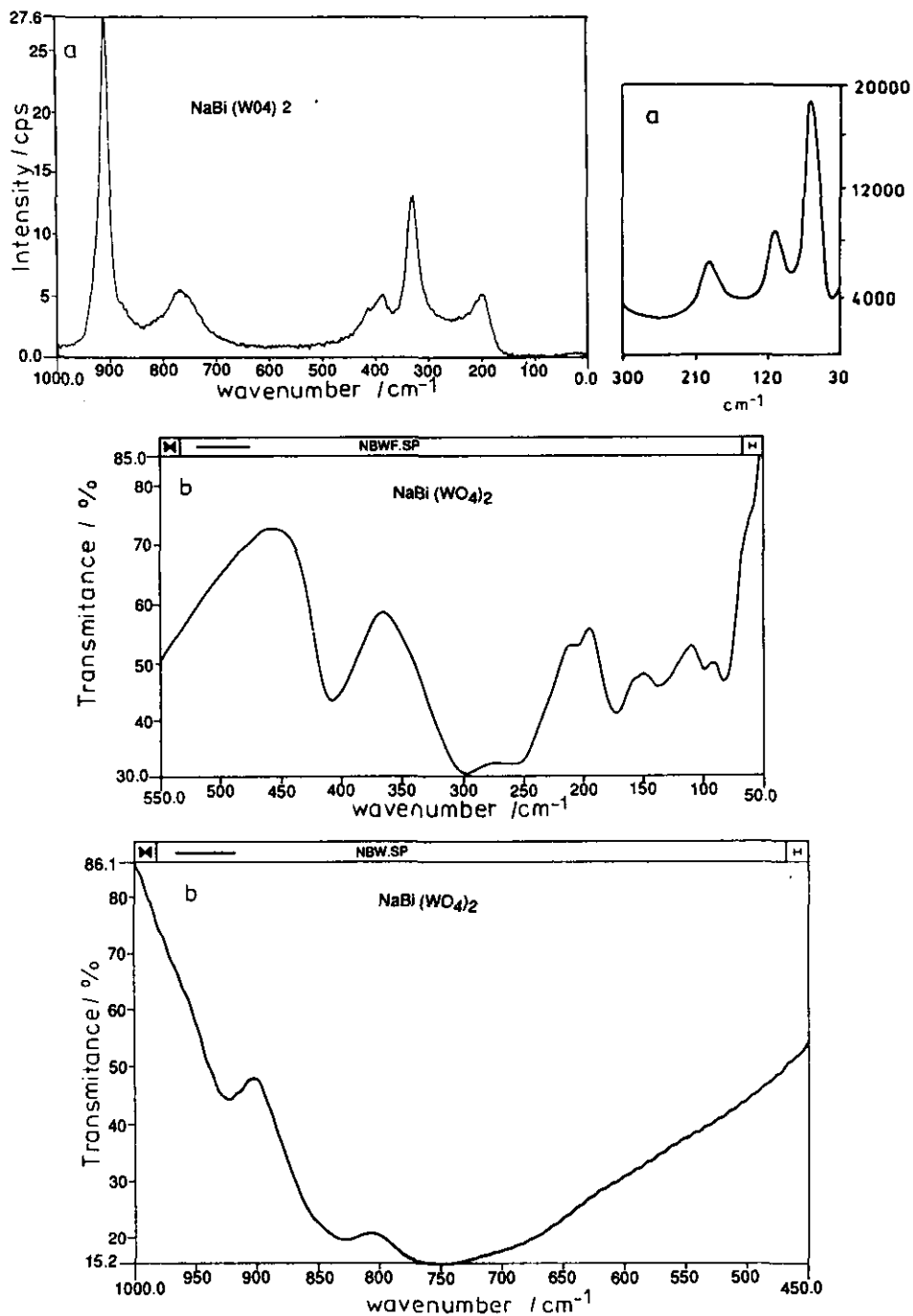
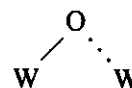
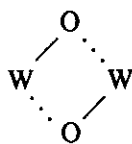


FIG. 1. Raman (a) and IR (b) spectra of  $NaBi(WO_4)_2$ .



a double oxygen bridge. The dimers are coupled to each other through

oxygen bridges forming a  $(W_2O_8)_n$  ribbon. For the factor group analysis the primitive cell with two nonequivalent  $KBi(WO_4)_2$  groups was selected. Since the wolframite-

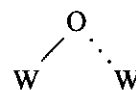
TABLE 3  
Factor Group Analysis for  $\text{LiBi}(\text{WO}_4)_2$  ( $P2/n$ ,  $Z = 2$ ),  $\text{NaCr}(\text{WO}_4)_2$  ( $P2/c$ ,  $Z = 2$ ), and  $\text{LiCr}(\text{WO}_4)_2$  ( $C2/c$ ,  $Z = 4$ )<sup>a</sup> Crystals

$C_{2h}$	$E$	$C_2(z)$	$i$	$\sigma_h$	Unit-cell modes					Activity	
					$n(N)$	$n(T)$	$n(T')$	$n(L)$	$n(\text{int})$	IR	Raman
$A_g$	1	1	1	1	17	0	2	1	14	—	XX, YY, ZZ, XY
$B_g$	1	-1	1	-1	19	0	4	1	14	—	XX, YY, ZZ, XY
$A_u$	1	1	-1	-1	17	1	4	0	12	Z	—
$B_u$	1	-1	-1	1	19	2	5	0	12	X, Y	—
					72	3	15	2	52		
$U_R(p)$	24	4	0	0							
$U_R(s)$	6	4	2	0							
$\chi_\rho(R)_N$	72	-4	0	0							
$\chi_\rho(R)_T$	3	-1	-3	1							
$\chi_\rho(R)_{T'}$	15	-3	-3	-1							

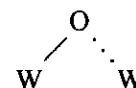
<sup>a</sup>  $\text{W}_2\text{O}_8^{4-}$  dimer of the  $C_i$  symmetry was chosen as the basic structural unit.

type crystals do not present true isolated molecular species, the FGA was carried out on the basis of the dimer structure. The results are presented in Table 5 and the spectra in Fig. 3. Vibrational frequencies are given in Table 6. The number of observed vibrations is somewhat larger than that obtained in the calculations. The reason for this is that our FGA does not take into account the

interactions between the dimers resulting in the formation of



single bridges. Nevertheless, we attempted to analyze the vibrational spectra on the basis of the dimer spectra plus weak perturbations corresponding to



interactions. The result will be discussed in Section 5.

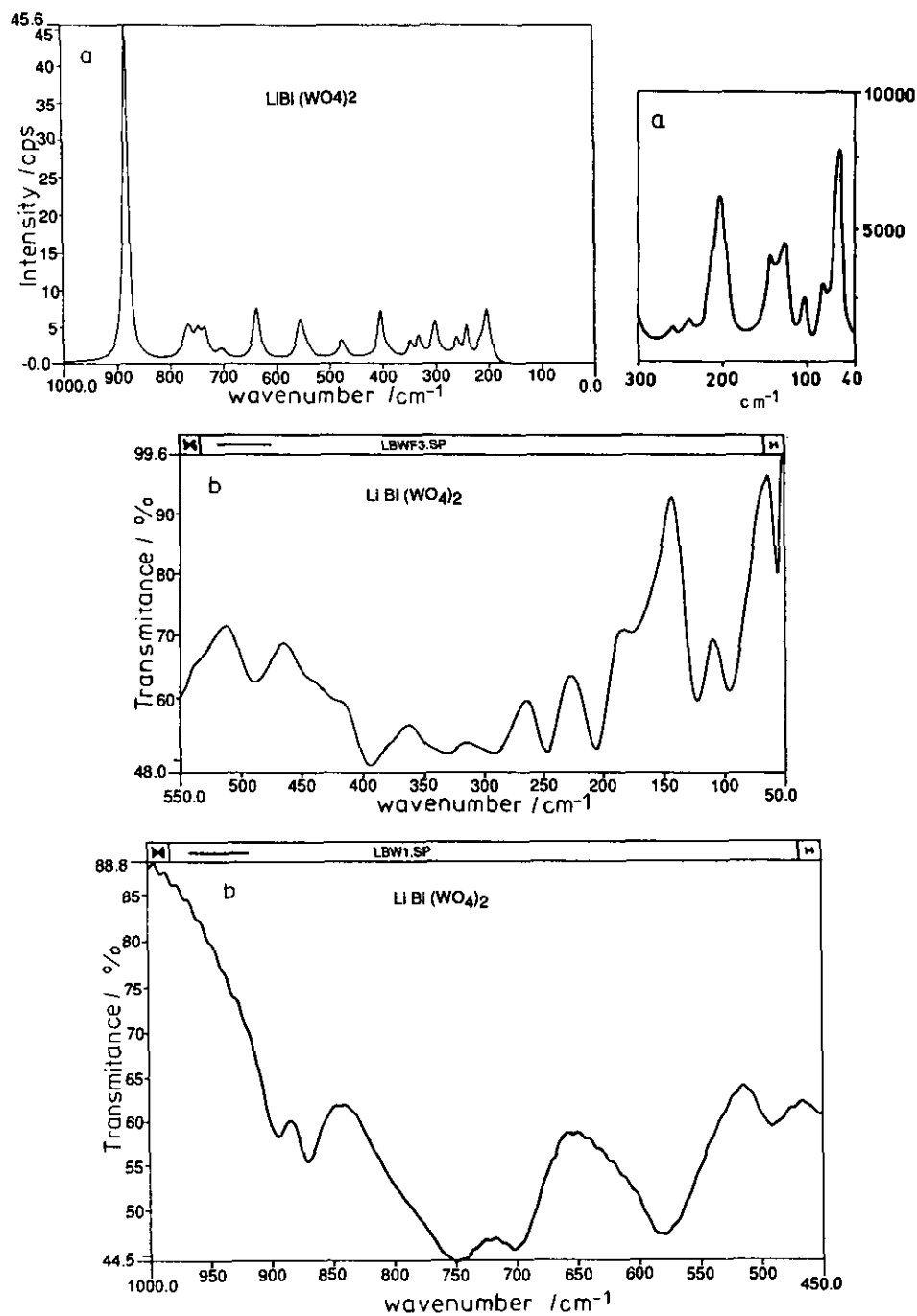
TABLE 4

IR and Raman Frequencies for Polycrystalline  $\text{LiBi}(\text{WO}_4)_2$

IR spectrum $u$ -phonons	Raman spectrum $g$ -phonons	Assignment	
893w	882vs	} $\nu_s(\text{WO}_6)$ Stretching modes	
870w			
793sh	765w	} $\nu_{as}(\text{WO}_6)$ and $\nu(\text{W}-\text{O}-\text{W})$ Stretching modes	
750s	746m		
	735w		
702s	702w		
578s	638w		
	554w		
	545sh		
490w	478w		
439sh			} $\delta_{as}(\text{WO}_6)$ Bending modes
420sh			
394m	404w		
331w	349w	} $\delta_s(\text{WO}_6)$ , $\delta(\text{W}-\text{O}-\text{W})$ Bending modes and $T'(\text{Li}^+)$	
292w	332w		
	302w		
246m	261w		
205m	242w		
	204m		
175w	142m		} $T'(\text{Bi}^{3+})$ and Torsional movements of the $(\text{W}_2\text{O}_8)_n$ chain
122s	125m		
96s	101w		
	77w		
56m	59m		

### 3.4. $\text{NaCr}(\text{WO}_4)_2$ and $\text{LiCr}(\text{WO}_4)_2$ Tungstates of the Wolframite-Type Structure

$\text{NaCr}(\text{WO}_4)_2$  crystallizes in the wolframite-type structure  $P2/c = C_{2h}^4$  with two formula units per unit cell, being isostructural to  $\text{NaIn}(\text{WO}_4)_2$ , for which  $a = 10.08$ ,  $b = 5.81$ ,  $c = 5.03$  Å, and  $\beta = 91.1^\circ$  (8–10).  $\text{LiCr}(\text{WO}_4)_2$  crystallizes in the  $C2/c = C_{2h}^6$  structure with four formula units per unit cell. This compound is isostructural to the wolframite-like  $\text{LiFe}(\text{WO}_4)_2$  compound with lattice parameters  $a = 9.26$ ,  $b = 11.38$ ,  $c = 4.91$  Å, and  $\beta = 90.3^\circ$  (9, 11). The structures and coordination numbers of alkali metal–chromium double tungstates are similar to those of  $\text{LiBi}(\text{WO}_4)_2$ . The coordination of tungsten ions is octahedral with  $\text{WO}_6$  distorted octahedra connected by a common edge and forming chains along the  $c$  axis. As in the wolframite-type compounds, the primitive cell contains two formula units; the number of vibrational modes and their activities are the same as for  $\text{LiBi}(\text{WO}_4)_2$  (Table 3). The observed vibrational frequencies are summarized in Table 7; the spectra are presented in Figs. 4 and 5.

FIG. 2. Raman (a) and IR (b) spectra of  $LiBi(WO_4)_2$ .

#### 4. X-RAY DIFFRACTION SPECTRA AND THEIR TEMPERATURE DEPENDENCE

The results of X-ray diffraction studies are listed in Table 8 for all compounds studied, except  $KBi(WO_4)_2$ . The spectrum for  $LiCr(WO_4)_2$  is in good agreement with that obtained for isostructural  $LiFe(WO_4)_2$  by Klevtsov and Kletsova (11). The purity of the samples studied was very good. The compounds are stable throughout a large

temperature range from 300 to 20 K and do not exhibit any phase transitions.

#### 5. DISCUSSION

##### 5.1. Internal Modes

According to structural criteria, the tungstates can be divided into three types.  $NaBi(WO_4)_2$  belongs to the first

TABLE 5  
Factor Group Analysis for  $\text{KBi}(\text{WO}_4)_2$  Crystals ( $C2/c$ ,  $Z = 4$ )<sup>a</sup>

$C_{2h}$	$E$	$C_2(b)$	$i$	$\sigma_h$	Unit-cell modes					Activity	
					$n(N)$	$n(T)$	$n(T')$	$n(L)$	$n(\text{int})$	IR	Raman
$A_g$	1	1	1	1	17	0	2	3	12	—	XX, YY, ZZ, XZ
$B_g$	1	-1	1	-1	19	0	4	3	12	—	XY, YZ
$A_u$	1	1	-1	-1	17	1	4	0	12	Y	—
$B_u$	1	-1	-1	1	19	2	5	0	12	X, Z	—
					72	3	15	6	48		
$U_R(p)$	24	4	0	0							
$U_R(s)$	6	4	2	0							
$U_R(s - v)$	2	0	2	0							
$\chi_p(R)_N$	72	-4	0	0							
$\chi_p(R)_T$	3	-1	-3	1							
$\chi_p(R)_T'$	15	-3	-3	-1							
$\chi_p(R)_L$	6	0	6	0							

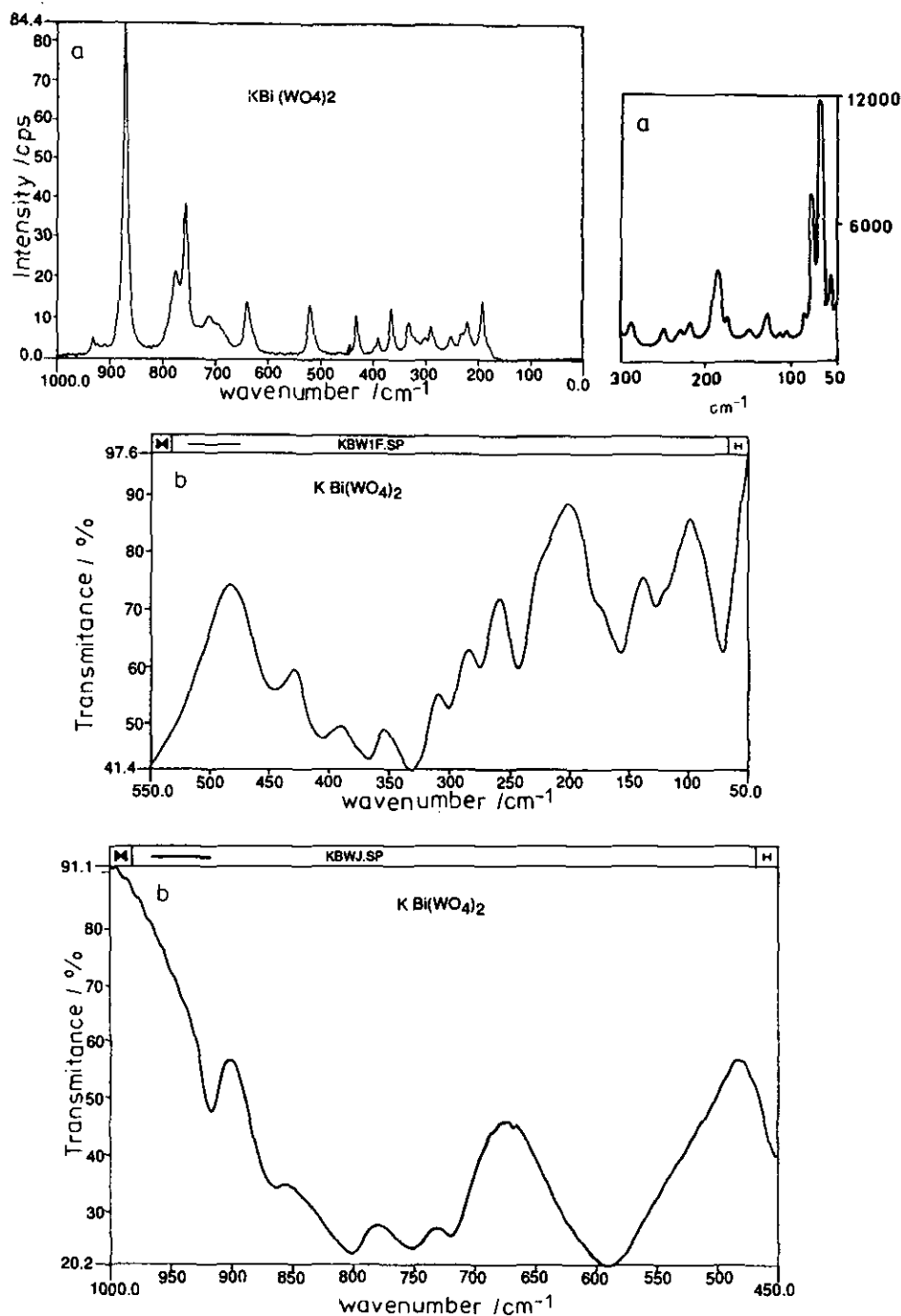
<sup>a</sup>  $\text{W}_2\text{O}_7^{4-}$  dimer of the  $C_i$  symmetry was chosen as the basic structural unit.

TABLE 6  
IR and Raman Spectra for Polycrystalline  $\text{KBi}(\text{WO}_4)_2$

IR spectrum $\mu$ -phonons	Raman spectrum $g$ -phonons	Assignment
917m	870vs	$\nu_s(\text{WO}_6)$ Stretching modes
863m		
802s		
752s	775m	
720m	756m	$\nu_{as}(\text{WO}_6)$ and $\nu(\text{W}-\text{O})$ and $\nu(\text{WOW})$ Stretching modes
	711w	
588s	697sh	
	638w	
450m	519w	$\delta_s(\text{WO}_6)$ , $\delta_{as}(\text{WO}_6)$ , $\delta(\text{W}-\text{O})$ and $\delta(\text{WOW})$ Bending modes
	431w	
405m	396sh	
377sh	391vw	
366s	365w	
330s	331w	
300w	299vw	
275w	289w	
	252vw	
244m	230vw	
	220w	$T'(K^+)$ and $L(\text{WO}_6)$ and $T'(W^{6+})$
	191w	
176sh	175vw	
155m	150vw	
127w	127w	
115vw	107vw	
	84vw	Probably $T'(Bi^{3+})$
81sh	77m	
71s	68m	
	57w	

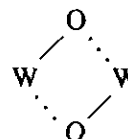
TABLE 7  
IR and Raman Spectra for Polycrystalline  $M^I\text{Cr}(\text{WO}_4)_2$  ( $M^I = \text{Na}, \text{Li}$ )

IR spectrum		Raman spectrum		Assignment
$M = \text{Na}$	$M = \text{Li}$	$M = \text{Na}$	$M = \text{Li}$	
948w	901m	946vs	921vs	$\nu_s(\text{WO}_6)$
882w		915w		
	844m	844s	782m	$\nu_{as}(\text{WO}_6)$ and $\nu(\text{W}-\text{O})$ and $\nu(\text{WOW})$ Stretching modes
761m		790sh		
	734s	773s	701w	
634s	653s	669w	676w	
608sh	615sh		625w	$\delta_s(\text{WO}_6)$ Bending modes
577sh	544sh	551w	551w	
545w	523m	515w	506vw	
473m	475w	459w	477vw	
	452sh		443vw	
415w	435m	419w	420m	
370sh	390s	363w	393m	$\delta_{as}(\text{WO}_6)$ , $\delta(\text{W}-\text{O})$ and $\delta(\text{WOW})$
			381w	
351s	363w	345w	355w	
340sh	331m	335w	329vw	
307sh	311sh	308w	300w	$T'(Na^+)$ , $T'(Li^+)$
301s	285sh	270m	277w	
265sh	270m		267vw	
250s	237m	225w	232m	
226vw	223sh			$T'(Cr^{3+})$
200w				
	195w			
147w	158w			
131vw				


 FIG. 3. Raman (a) and IR (b) spectra of  $KBi(WO_4)_2$ .

type, scheelite compounds which consists of the isolated  $WO_4^{2-}$  ions in the unit cell. The wolframite-type compounds form another modification ( $\beta$ - $LiBi(WO_4)_2$ ,  $NaCr(WO_4)_2$ ,  $LiCr(WO_4)_2$ ) with a relatively high degree of condensation of oxygen ions around the  $W^{6+}$  ions and with dense packing of the coordination polyhedra in the unit cell. The resulting  $CN(W^{6+})$  equals 6 because the tungstate ions are additionally connected to each other

by means of intermolecular interactions of the



type. The resulting coordination octahedron  $WO_6^{6-}$  is

TABLE 8  
X-Ray Diffraction Data for NaBi(WO<sub>4</sub>)<sub>2</sub>, LiBi(WO<sub>4</sub>)<sub>2</sub>, NaCr(WO<sub>4</sub>)<sub>2</sub>, and LiCr(WO<sub>4</sub>)<sub>2</sub>

NaBi(WO <sub>4</sub> ) <sub>2</sub>			LiBi(WO <sub>4</sub> ) <sub>2</sub>			NaCr(WO <sub>4</sub> ) <sub>2</sub>			LiCr(WO <sub>4</sub> ) <sub>2</sub>					
<i>d</i>	2θ	<i>I</i>	<i>d</i>	2θ	<i>I</i>	<i>d</i>	2θ	<i>I</i>	<i>d</i>	2θ	<i>I</i>	<i>d</i>	2θ	<i>I</i>
4.811	18.427	10.0	6.118	14.465	3.6	8.067	10.958	58.8	5.661	15.641	12.8	1.845	49.363	3.5
3.136	28.423	100.0	6.034	14.668	20.5	6.089	14.534	1.7	4.736	18.722	2.1	1.811	50.354	2.2
2.882	31.006	15.7	5.172	17.130	4.5	4.562	19.440	1.5	4.601	19.276	100.0	1.809	50.417	2.5
2.644	33.872	27.6	4.996	17.737	4.9	4.485	19.777	1.7	4.046	21.948	3.1	1.789	51.004	12.0
2.091	43.227	5.5	4.519	19.630	2.8	4.413	20.106	2.1	4.031	22.030	3.5	1.783	51.178	6.0
2.013	45.007	4.5	4.385	20.235	5.3	4.052	21.918	100.0	4.013	22.135	3.4	1.750	52.235	18.9
1.947	46.602	36.1	3.852	23.069	7.0	3.800	23.391	2.7	3.696	24.057	54.7	1.744	52.414	8.6
1.869	48.687	22.7	3.348	26.606	2.0	3.772	23.567	5.4	3.573	24.899	46.3	1.721	53.163	4.7
1.708	53.615	20.1	3.091	28.859	7.7	3.654	24.339	6.3	3.493	25.481	3.6	1.714	53.419	5.1
1.605	57.35	36.1	3.024	29.516	100.0	3.485	25.535	5.6	3.181	28.024	3.6	1.683	54.463	27.6
1.567	58.873	10.0	3.005	29.703	15.1	3.228	27.610	6.3	3.156	28.251	4.7	1.677	54.671	21.2
1.321	71.320	7.7	2.922	30.566	4.0	3.053	29.225	2.7	3.108	28.697	2.1	1.670	54.922	10.7
1.264	75.082	35.5	2.895	30.865	6.9	2.706	33.079	51.9	3.100	28.779	2.5	1.565	58.964	4.7
1.260	75.357	8.4	2.586	34.666	6.3	2.478	36.222	6.8	2.893	30.884	71.1	1.561	59.145	3.0
			2.504	35.827	4.9	2.032	44.542	2.4	2.873	31.107	52.5	1.536	60.174	4.6
			2.488	36.063	4.8	1.826	49.891	1.7	2.833	31.549	16.3	1.532	60.351	2.4
			2.279	39.501	2.1	1.682	54.523	3.9	2.453	36.610	18.2	1.495	62.007	4.8
			2.018	44.886	4.1	1.677	54.701	1.9	2.442	36.779	16.1	1.491	62.193	2.7
			1.923	47.216	2.0	1.627	56.530	12.7	2.416	37.189	16.0	1.486	62.456	8.1
			1.872	48.587	11.1	1.622	56.707	7.1	2.406	37.349	5.0	1.482	62.631	5.9
			1.783	51.190	2.1	1.578	58.451	1.7	2.306	39.053	17.1	1.478	62.801	7.0
			1.514	61.151	6.8	1.572	58.664	2.0	2.295	39.218	6.0	1.475	62.986	3.4
			1.507	61.491	2.1	1.381	67.810	1.6	2.163	41.732	36.7	1.462	63.577	6.3
			1.497	61.927	3.2	1.356	69.245	6.4	2.135	42.290	4.4	1.458	63.762	3.3
			1.487	62.390	1.9	1.352	69.445	3.5	2.091	43.237	4.6	1.448	64.289	3.4
			1.456	63.866	2.2				2.087	43.317	5.3	1.444	64.475	2.2
			1.449	64.230	4.2				2.023	44.752	4.5	1.439	64.740	3.5
									2.017	44.903	2.7	1.420	65.710	13.3
									2.011	45.051	5.4	1.416	65.911	13.8
									1.962	46.225	12.5	1.412	66.108	12.3
									1.951	46.518	14.3	1.409	66.303	4.1
									1.891	48.063	5.4			
									1.886	48.222	2.6			
									1.851	49.186	7.9			

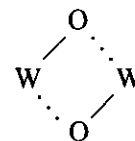
strongly distorted. In the  $M^I M^{III}(WO_4)_2$  double tungstates of wolframite type, cation localization may occur in three ways:

A. The  $M^I$  ion is surrounded in the second coordination sphere by four  $M^{III}$  ions forming a structure of the  $\beta$ -LiYb(WO<sub>4</sub>)<sub>2</sub> type (7). LiBi(WO<sub>4</sub>)<sub>2</sub> is an example of such an arrangement.

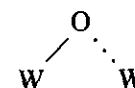
B. Each  $M^I$  cation is surrounded in the second coordination sphere by  $2M^I$  and  $2M^{III}$  ions characteristic of the LiFe(WO<sub>4</sub>)<sub>2</sub> modification (9, 11). LiCr(WO<sub>4</sub>)<sub>2</sub> crystallizes in this structure.

C. Each  $M^I$  or  $M^{III}$  cation is surrounded in the plane by cations of the same type, giving laminated or layered structures. These wolframites are isostructural to the NaIn(WO<sub>4</sub>)<sub>2</sub> (8–10) and NaFe(WO<sub>4</sub>)<sub>2</sub> (10). Of the compounds studied, NaCr(WO<sub>4</sub>)<sub>2</sub> is of this type.

Apart from the scheelite- and wolframite-type tungstates studied in the present work, the monoclinic KBi(WO<sub>4</sub>)<sub>2</sub> forms the third type of compound isostructural to  $\alpha$ -KY(WO<sub>4</sub>)<sub>2</sub> (4, 5) (see Section 3.3 of this work). This tungstate may be considered a three-dimensional polymeric system in which in part of the

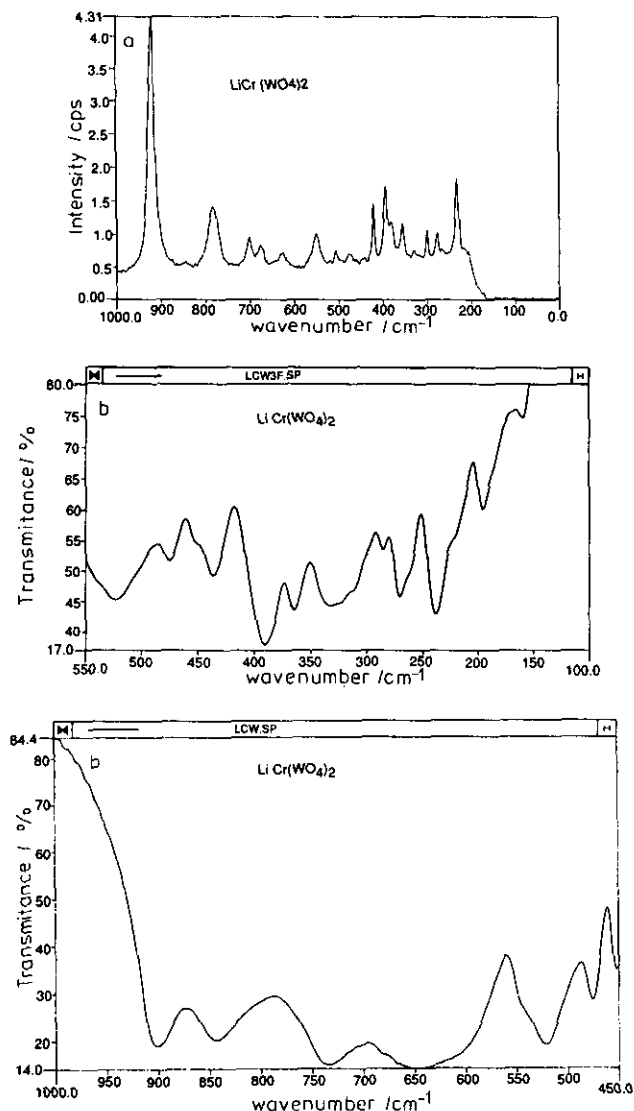


bridge bond



interactions also occur.

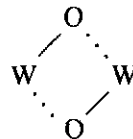


FIG. 4. Raman (a) and IR (b) spectra of  $LiCr(WO_4)_2$ .

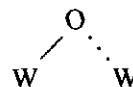
The vibrational spectra of the compounds described above distinctly differ from one type to another. Table 9 compares the vibrational characteristic of these compounds.

During the past 30 years many papers have been published on the vibrational properties of tungstates. The isolated  $WO_4^{2-}$  ion has  $T_d$  symmetry with four fundamental vibrations at  $\nu_1(A_1)$  928,  $\nu_2(E)$  320,  $\nu_3(F_2)$  833, and  $\nu_4(F_2)$  405  $cm^{-1}$  (12, 13). Studies of solid tungstates provide much information on their vibrational levels (14–35). For the alkaline earth tungstates, the stretching vibrations are observed in the region 750–930  $cm^{-1}$  while bending vibrations  $\nu_2$  and  $\nu_4$  are in the 300–440  $cm^{-1}$  range (14–17, 19, 23, 25, 26, 31, 32). In the case of  $Al_2(WO_4)_3$  these regions are 770–1080 and 280–470  $cm^{-1}$ , respectively (35). Studies of the systems containing  $WO_6$  octahedra ( $Ba_3WO_6$ , perovskite-type  $Ba_2MgWO_6$ , and  $Ba_2CaWO_6$ , and many oth-

ers) showed that the stretching region extends to 580–910  $cm^{-1}$  (18, 21, 22, 24, 27–29). Further single crystal studies of  $\alpha$ - $KY(WO_4)_2$  and  $KDy(WO_4)_2$  crystallizing in the structures containing both double



bridge systems and single



bridges revealed  $\nu_1$  and  $\nu_3$  region in the range 530–935

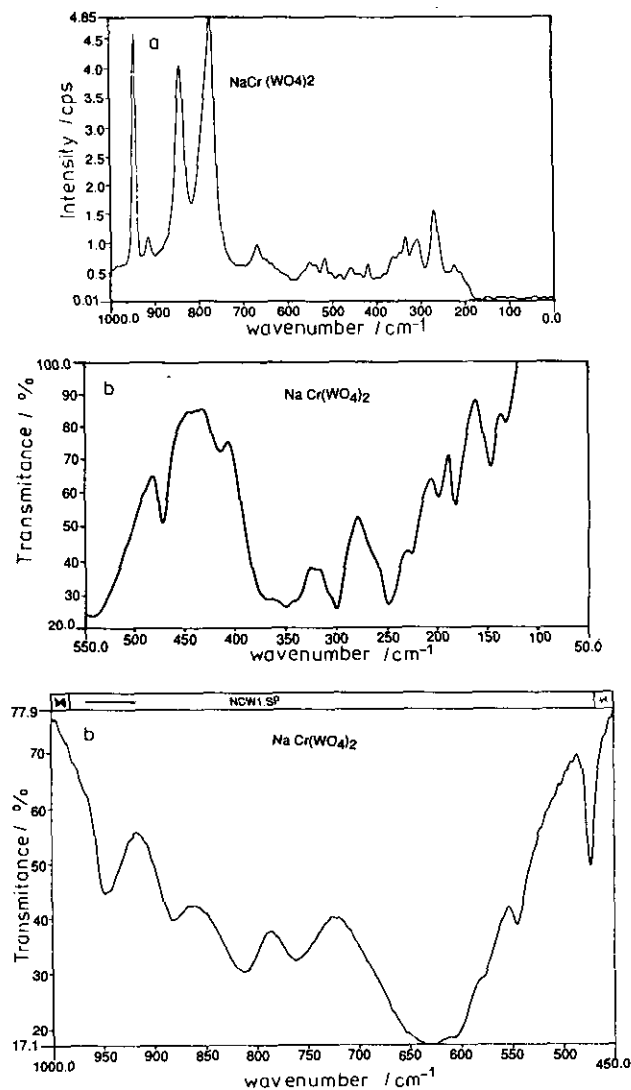
FIG. 5. Raman (a) and IR (b) spectra of  $NaCr(WO_4)_2$ .

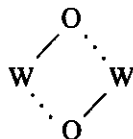
TABLE 9  
The Comparison of the Vibrational Data for Scheelite and Wolframite Type  $M^I M^{III}(\text{WO}_4)_2$  Crystals

Scheelite type compounds				Wolframite type compounds and $\text{KBi}(\text{WO}_4)_2$			
Atom	SS	CN	Representation	Atom	SS	CN	Representation
M	$C_2$	8		M	$C_2$	6	$A_g + 2B_g + A_u + 2B_u$
X	$C_2$	8	$B_g + E_g + A_u + E_u$	X	$C_2$	6	$A_g + 2B_g + A_u + 2B_u$
W	$S_4$	4	$A_g + B_g + 2E_g + A_u + B_u + 2E_u$	W	$C_1$	6	$3A_g + 3B_g + 3A_u + 3B_u$
O	$C_1$	1	$2A_g + 3B_g + 2E_g + 3A_u + 2B_u + 2E_u$	O	$C_1$	1, 2	$12A_g + 12B_g + 12A_u + 12B_u$
$\Gamma_{\text{vib}} = 3A_g + 5B_g + 5E_g + 5A_u + 3B_u + 5E_u$				$\Gamma_{\text{vib}} = 17A_g + 19B_g + 17A_u + 19B_u$			
$\Gamma_{\text{ac}} = A_u + E_u$				$\Gamma_{\text{ac}} = A_u + 2B_u$			
$\Gamma_{\text{vib opt}} = 3A_g + 5B_g + 5E_g + 4A_u + 3B_u + 4E_u$				$\Gamma_{\text{vib opt}} = 17A_g + 19B_g + 16A_u + 17B_u$			

Note. SS, site symmetry; CN, coordination number.

$\text{cm}^{-1}$  and  $\nu_2$  and  $\nu_4$  in the range 277–500  $\text{cm}^{-1}$  (33, 34). Single crystal studies and calculations showed also that  $\nu_1 > \nu_3$  and  $\nu_2 < \nu_4$  (17, 20, 26, 30). For some compounds,  $\nu_2$  and  $\nu_4$  levels overlap and some of the  $\nu_2$  components may lie above  $\nu_4$  (32). In addition, a strong coupling exists between the internal and external modes (31, 32).

Data from the very rich literature enabled us to describe the internal modes of the compounds studied. The most intensive lines in the Raman spectra fall in the range 870–946  $\text{cm}^{-1}$  and in the IR spectra in the range 523–828  $\text{cm}^{-1}$ . From the intensity rule (36, 37) ( $\nu_1$  has higher intensity than  $\nu_3$  in Raman spectra and the reverse in IR spectra) we can assign bands in the region 870–946  $\text{cm}^{-1}$  as symmetric stretching vibrations. The number of totally symmetric vibrations should be equal to the number of  $\text{WO}_4$  units present in the primitive unit cell. These units can be subdivided into sets of crystallographically equivalent molecules, which vibrate with the same energy. In this case the number of  $\nu_1$  lines in the spectra reflects the number of nonequivalent sites present in the crystal. This is approximately true for the compounds studied. These lines fall in the range 870–950  $\text{cm}^{-1}$ . The asymmetric stretching vibrations are observed in the range 740–880  $\text{cm}^{-1}$ . Moreover, for tungstates, where the

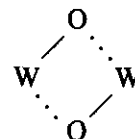


bridge system exists in the unit cell (all compounds studied except for  $\text{NaBi}(\text{WO}_4)_2$ ) we observe very large splitting of the  $\nu_3$  stretching mode (about 350  $\text{cm}^{-1}$ ). The bending vibrations, for the compounds studied, fall in the range 275–490  $\text{cm}^{-1}$ . Miller *et al.* (37) have shown that  $\nu_2$  has a higher intensity than  $\nu_4$  in Raman spectra and the reverse in IR spectra. This condition is well satisfied for Raman spectra but not satisfied in the case of IR spectra of Na-

$\text{Bi}(\text{WO}_4)_2$  and  $\text{KBi}(\text{WO}_4)_2$ . For these two systems, the intensity of  $\nu_2$  is higher than  $\nu_4$  in IR spectra.

The vibrational characteristics in the internal mode region prove full agreement between the structure of the compounds under study and their phonon properties. The scheelite-type derivatives reveal in this region two patterns corresponding to the stretching ( $\nu$ ) and bending ( $\delta$ ) modes of the  $\text{WO}_4^{2-}$  ion. Both patterns are divided into two subgroups  $\nu_{1,2}$  and  $\delta_{2,4}$  as predicted by the group-theoretical analysis. The distinct gap in the region of 420–740  $\text{cm}^{-1}$  in the energy distribution of the  $\bar{k} = 0$  phonons is clearly observed in the spectra of the scheelite-type  $\text{NaBi}(\text{WO}_4)_2$  compound. The comparison of vibrational patterns corresponding to the scheelite-type and wolframite-type compounds reveals the following differences in the internal mode region:

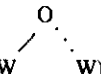
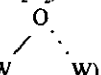
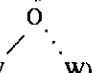
- the number of lines is doubled due to the splitting of pertinent bands into two components;
- additional bands arise in the “energy gap region” due to the



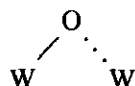
intermolecular interactions in the wolframite-type unit cell.

The method of ascent in symmetry allows us to describe the vibrations of the  $\text{W}_2\text{O}_2$  bridge system in terms of  $C_i$  symmetry. Such a four-nuclear system has six vibrational degrees of freedom, which can be classified as stretching  $\nu_1(A_u)$ ,  $\nu_2(A_g)$ ,  $\nu_3(A_u)$ , and  $\nu_4(A_g)$  modes and bending  $\nu_5(A_u) + \nu_6(A_g)$  modes. The comparison of the spectra obtained for scheelite-type  $\text{NaBi}(\text{WO}_4)_2$  and for the remaining compounds allows us to propose in Table 10 the assignment of the most characteristic bands to the respective modes of the  $\text{W}_2\text{O}_2$  bridge system.

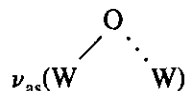
TABLE 10  
The Phonon Assignment in the Internal Mode Region

Vibrational modes	NaBi(WO <sub>4</sub> ) <sub>2</sub>	LiBi(WO <sub>4</sub> ) <sub>2</sub>	NaCr(WO <sub>4</sub> ) <sub>2</sub> LiCr(WO <sub>4</sub> ) <sub>2</sub>	KBi(WO <sub>4</sub> ) <sub>2</sub>
$\nu_1^t(WO_4)$	907–927	870–893	882–948	863–917
$\nu_2^t(WO_4)$	860–880			
	815–828			
	740–770	735–793	734–844	752–775
 $\nu_{as}^1(W-O-W)$	—	—	—	802
$\nu_{as}^1(W_2O_2)$	—	702	634–701	697–720
$\nu_{s}^1(W_2O_2)$	—	638	608–625	638
$\nu_{s}^1(W_2O_2)$	—	545–578	506–577	519–588
$\nu_{as}^1(W_2O_2)$	—	478–490	452–477	431–450
 $\nu_{s}^2(W-O-W)$	—	—	—	365–366
$\nu_{s}^2(WO_4)$	386–414	394–439	363–435	377–405
$\nu_2^t(WO_4)$	254–328	292–332	285–363	289–331
 $\delta(W-O-W)$	—	—	—	220–230
$\nu_{s}^2(W_2O_2)$	—	261	265–277	252
$\nu_{s}^2(W_2O_2)$	—	246	223–237	244

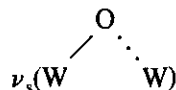
As mentioned above, the  $KBi(WO_4)_2$  unit cell contains additional



bridge bonds and therefore some distinct lines in the internal mode region can be assigned to this structural fragment. Particularly characteristic are strong bands near 802 and 365  $cm^{-1}$ , which we assign to the



and



modes, respectively (Table 10).

### 5.2. Optical External Phonons

In the far-infrared region translational modes  $T'(M^+)$ ,  $T'(X^{3+})$ ,  $T'(WO_4^{2-})$ , and librational modes  $L(WO_4^{2-})$  are

expected. Studies of scheelite-type compounds (14, 15, 19, 23, 25, 31, 32) have shown that the frequencies of the translational modes are approximately proportional to the square root of the appropriate reciprocal reduced masses. For simple  $MWO_4$  tungstates ( $M = Ca, Sr, Ba, \text{ and } Pb$ ) the translational vibrations  $T'(M^{2+})$  are observed at 207–210, 162–163, 141–142, and at 126  $cm^{-1}$ , respectively (19, 25, 26, 31, 32). For potassium rare earth double tungstates  $T'(K^+)$  modes are observed in the range 230–280  $cm^{-1}$  (33, 34). According to (25, 26), for  $CaWO_4$  translational modes,  $T'(WO_4^{2-})$ , are observed in Raman spectra at 83–87  $cm^{-1}$  and 115–117  $cm^{-1}$ . Akimov suggests (31) that these lines occur at 150 and 74  $cm^{-1}$ . We agree with this assignment and therefore we assign the IR bands at 81–130  $cm^{-1}$  to  $T'(WO_4^{2-})$ . Generally speaking the exchange of the  $M^+$  ( $Li^+, Na^+, K^+$ ) and  $M^{3+}$  ( $Bi^{3+}, Cr^{3+}$ ) ions in  $M^+M^{3+}(WO_4)_2$  complexes causes a frequency shift of translational modes toward smaller wave numbers. Such behavior is particularly evident in the IR spectra. These changes allow us to propose the assignment of the  $T'(M^+)$  and  $T'(M^{3+})$  phonons in the following way:  $T'(Li^+)$  190–210  $cm^{-1}$ ;  $T'(Na^+)$  170–190  $cm^{-1}$ ;  $T'(K^+)$  150–160  $cm^{-1}$ ;  $T'(M^+, Cr^{3+})$  coupled modes 110–170  $cm^{-1}$ ;  $T'(Bi^{3+})$  60–100  $cm^{-1}$ . This assignment of the vibrational bands to “localized” motions is only an oversimplified scheme. Our earlier results (34), as well as those of other authors (38), suggest that the translation of the  $M^+$ ,  $M^{3+}$ , and  $M^{6+}$  ions are strongly coupled and should be described as mixed  $T'(M^+, M^{6+})$  and  $T'(M^{3+}, M^{6+})$  translatory lattice modes. The librational modes for  $CaWO_4$  were observed between 195–290  $cm^{-1}$  (14, 15, 19, 23, 25, 31, 32). These modes are observed in our spectra of  $NaBi(WO_4)_2$  in the range 193–254  $cm^{-1}$ . Our former studies of polymeric tungstates (33, 34) demonstrated, however, that for compounds where a polymeric oxy, system is formed, the librational modes could be lowered.

For a detailed identification of the modes, polarization measurements are needed. These studies will be presented in our next paper.

The compounds studied are stable in the wide temperature range from 300 to 20 K and do not exhibit any phase transitions. In view of the stability of  $M^1Bi(WO_4)_2$  crystals as host lattices for  $Cr^{3+}$  ions, this point is very important. From crystal growth considerations, the  $NaBi(WO_4)_2$  matrix melts congruently, and no phase transitions occur during cooling to helium temperature (3, 6). The potassium and lithium derivatives decompose during fusion. Chemical stability in a humid environment is their attribute. From the spectroscopic point of view the  $Cr^{3+}$  ions must be coordinated octahedrally by the oxygen ions. This also holds true for the trivalent  $Bi^{3+}$  sites of the compounds studied. Because of the arguments presented in this paper,  $M^1Bi_{1-x}Cr_x(WO_4)_2$  type compounds are expected to be prospective quantum generators.

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